

# **THE CHARACTERIZATION OF ENERGY TRANSFER IN HIGH SPEED GAS FLOWS**

An Undergraduate Research Scholars Thesis

by

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## ABSTRACT

### The Characterization of Energy Transfer in High-Speed Gas Flows

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Vibrationally Excited Nitric Oxide Monitoring (VENOM)<sup>14</sup> is a technique which utilizes the electronic excitation of the tracer molecule NO in high speed gas flows to make simultaneous velocity and temperature measurements. The ability to model these flows using the Navier-Stokes turbulence equations is vital for the continued growth in both chemical and aerospace fields. This technique increases the accuracy of the predictions made using these equations by allowing both temperature and velocity measurements to be made using a single technique. Presented here is the expansion of the technique to three component velocity using the invisible ink method.<sup>13</sup> The fluorescence lifetime is affected based on the composition of the flow. In order to understand the effects of quantized energy being inserted into the flow, the quenching behavior of benzene and C<sub>6</sub>F<sub>6</sub> on the fluorescence lifetime was studied. Presented here is the use of the near resonance energy transfer model as opposed to the harpoon model for predicting collisional quenching cross sections.<sup>11</sup>

## **DEDICATION**

This research proposal is dedicated to the people who have supported me throughout my years of undergraduate research, particularly my family, my fiancée Ashley Eckenrode, and Dr. Simon North. Without him, and the entire North group, none of this would have would not have been possible.

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## NOMENCLATURE

VENOM	Vibrationally Excited Nitric Oxide Monitoring
PLIF	Planar Laser Induced Fluorescence
MTV	Molecular Tagging Velocimetry
SHR	Supersonic High Reynolds Number Tunnel
RPHT	Repetitively Pulsed Hypersonic Test Cell
TNE	Thermal Non-Equilibrium

# CHAPTER I

## INTRODUCTION

The study of turbulence and non-equilibrium flows is important to both chemistry and aerospace challenges facing scientists today. Studies have been done to quantify the coupling between energy transfer and velocity and temperature changes in high speed gas flows. Techniques such as molecular tagging velocimetry (MTV) and planar laser induced fluorescence (PLIF) are well studied techniques used to measure the velocity and temperature respectively in turbulent flow fields in which allow for modeling of these systems. MTV utilizes a tagging molecule, such as nitric oxide (NO), which has fluorescent properties which can be excited using a laser as an energy source. A time delay is then utilized to obtain the velocity of the molecules via the displacement of a fluorescent grid. PLIF also utilizes a tracer molecule but instead of measuring the change in position, the fluorescence intensity difference between two different rotational states is measured. By taking a ratio of the intensity at a high and low populated band, a temperature map of the flowfield is obtained. Vibrationally excited nitric oxide monitoring (VENOM) is a technique which has been previously demonstrated by this group to combine the theories behind PLIF and MTV in order to be able to simultaneously obtain both temperature and velocity measurements.<sup>14,15</sup> By obtaining both measurements from a single excitation event, the coupling between the two terms can be fully understood. This allows for more accurate experimental data which can be used in order to create better models for these types of systems.

The original VENOM technique<sup>15</sup> utilizes the photodissociation of NO<sub>2</sub> to provide a excited population of NO. For the photodissociation method, a 355 nm laser grid is used to photodissociate NO<sub>2</sub> and create a population of NO (X,v=1). This creates a “write” grid in the

flow of NO ( $v=1$ ) and this is then probed by a 225 nm laser sheet probing the  $A\ ^2\Sigma^+_{1/2} (v' = 1) \leftarrow X\ ^2\Pi_{1/2} (v = 1)$  band of NO. The photoproducts of the initial dissociation are the only thing being probed because there is minimal population of  $v=1$  NO to at room temperature. The population is unlikely to exceed 0.01%. By using two “read” laser sheets tuned to the  $R_1 + Q_{21}$  line and one to the  $R_1 + Q_{21}$  line respectively, simultaneous measurements of temperature and velocity can be obtained.

An issue affecting techniques such as MTV, PLIF, and VENOM is the rate of fluorescence quenching of NO, the tracer species, utilized in laser induced fluorescence (LIF). NO is used as a tracer molecule because it creates only minimal perturbation of the flow. Understanding the rate constants of different quenching molecules such as  $C_6H_6$  or  $C_6F_6$  is necessary for proper analysis of the LIF signal obtained.<sup>10</sup> In order for the energy transfer from the NO to the quencher to be efficient the latter has to have a relatively high electron affinity when using the charge transfer model. Benzene and its derivatives are of interest because changes in the atoms attached to the ring provide changes in electronegativity and electronic structure. These changes then change the curve crossing rates. When making a comparison between benzene and  $C_6F_6$  for example, the latter has a higher electron affinity and a slight difference in the A-state energy. The A-state energy for  $C_6H_6$  is 4.9 eV while that of  $C_6F_6$  is 4.8 eV. If NO ( $A^2\Sigma^+$ ) quenching by these molecules takes place via the charge transfer model then their cross sections should indicate an electron affinity dependence. Haas and Greenblatt<sup>3</sup> obtained quenching cross section measurements that were larger than those obtained here and could be predicted using the harpoon mechanism. It was proposed that an electronic resonant energy transfer process might better describe the interaction between NO and benzene.



Thermal non-equilibrium is present in hypersonic flow fields and plays a significant role in changes in the flow properties. The thermal non-equilibrium (TNE) changes present within high speed gas flow fields and the energy transfers between vibrational, translational, and rotational levels happen at varying magnitudes and time scales which is why it is important to understand the effects of the tracer molecules being used to study the system. The creation of more accurate modeling of these tracers allows for them to be used in laser induced non-equilibrium studies (LINE) and in the continued efforts by aerospace engineers to improve hypersonic flight and better handle the effects of reentry on capsules returning from out of earth's orbit. Methods which allow for accurate spatial measurements of both temperature and velocity allow for more accurate modeling and therefore more efficient vehicles to be designed.

## CHAPTER II

### EXPERIMENTAL

#### Spectroscopic VENOM

There are two variations of the VENOM technique, one using photodissociation of  $\text{NO}_2$ , and one which electronically excites NO via spontaneous emission and collisional quenching. The latter, known as invisible ink, limits the perturbation of the flow with thermal non-equilibrium and allows for more accurate thermometry measurements to be made. The invisible ink variation is described below and will be utilized over the photodissociation method for its improvement on thermometry measurements.

The VENOM technique was performed in the repetitively pulsed hypersonic test (RPHT) test cell in figure 1 pumped down using Leybold E250 rotary pump and a roots blower pump assembly with a pumping speed of  $\sim 250$  cfm coupled through a vacuum line. A converging-diverging de Laval nozzle at Mach 4.6 was used to produce the pulsed hypersonic flow with a temperature that is  $\sim 52$  K. A MKS Series 902 pressure transducer was used to measure the

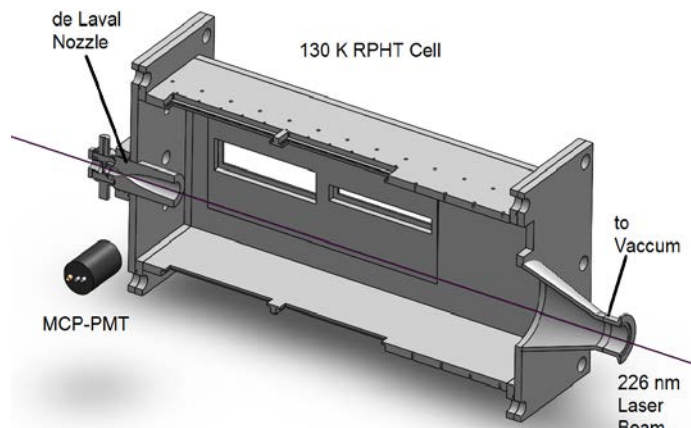


Figure 1: Repetitively pulsed hypersonic test used to obtain the spectroscopic measurements discussed here<sup>11</sup>

pressure continuously within the test cell. The settling region has a volume of  $2.25 \text{ cm}^3$  with the gas being injected using pulse valves operating at a speed of 10Hz.

The gas mixture is a ratio of 5% NO in  $\text{N}_2$  and is maintained using MKS Mass-Flo 1179A mass flow controllers. These are controlled by a four-channel power supply.

Using a system of lasers, (Figure 2) the “write” laser excited the  $R_1 + Q_{21}$  bandhead of the  $A^2\Sigma^+_{1/2} (\nu' = 0) \leftarrow X^2\Pi_{1/2} (\nu = 0)$  band near 225nm. A beam splitter is used to split the write

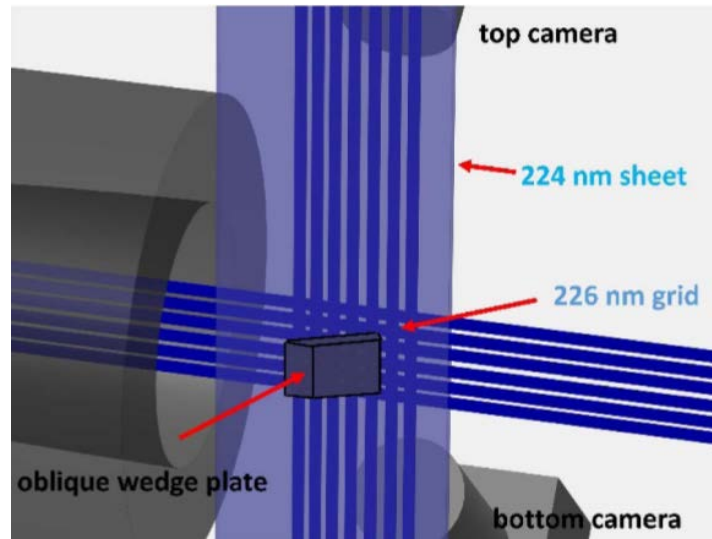


Figure 2: laser beam set up showing the intersecting lines and the probe beam<sup>13</sup>

beam into two 50% portions and sent through aluminum meshes in order to create a modulation of lines. The modulated beams are then passed through the cell perpendicular to each other outside the nozzle. The “read” lasers are tuned to the  $A^2\Sigma^+_{1/2} (\nu' = 1) \leftarrow X^2\Pi_{1/2} (\nu = 1)$  band on the  $R_1 + Q_{21}$  (1.5) and  $R_1 + Q_{21}$  (8.5) lines with time delays at both 1.2 and 1.6  $\mu\text{s}$  after the “write” pulse. This is necessary to allow for both sufficient grid displacement to be able to calculate velocity and allows for the fluorescence from the first excitation to decay. Two of the same laser system, fitted with an injection-seeded Spectra Physics PRO-290-10 Nd:YAG laser were operated at 10 Hz pumping at 532 nm and a Sirah Cobra Stretch pulsed dye laser to

produce a  $\sim 607$  nm output using a solution of Rhodamine 610 and Rhodamine 640 in methanol. The dye output is mixed with the residual 355 nm from the Nd:YAG laser in a Sirah SFM-355 nm frequency. The images are collected using two PI-MAX4 ICCD cameras fitted with CERCO 100 mm UV lenses and extension rings immediately after the “write” laser.

The stereoscopic VENOM technique produces three component velocity using two ICCD cameras in addition to the original camera at  $40.5^\circ$  and  $-38.7^\circ$ . Two “read” lasers are utilized as before but the images are dewarped with respect to a reference image to obtain the out of plane movement. The out of plane measurement was performed using a stainless-steel wedge which enabled a known out of plane measurement to be made.

## **Quenching**

The use of nitric oxide (NO) as a tracer molecule is a well-studied technique. It has been applied in the VENOM technique as a method of simultaneously measuring temperature and velocity in a high-speed gas flow-field. This technique monitors rotational temperature and does not examine vibrational temperature. The two competing pathways of fluorescence and collisional quenching produce different amounts of rotationally excited NO. In order to be able to fully characterize the flowfield and ensure accurate temperature readings are being collected a complete understanding of excitation pathways is necessary.

Thermally averaged collisional quenching cross sections from the fluorescence of NO ( $A^2\Sigma^+$ ) by  $C_6H_6$  and  $C_6F_6$  were obtained by fitting the rate constants for the fluorescence decay at different concentrations of the quenching molecule. The 300 K measurements were performed in a custom-built cell for flows less than 200 sccm as shown in figure 3. The temperature was maintained using heating tape wrapped around the cell and was monitored with an internal thermocouple. A Ruvac WS1001US Roots blower with a Beybold D65B backing pump was used

to vacuum down the cell. Optical access was obtained using UV grade fused silica windows. The gas mixtures were controlled using MKS Mass-Flo 1179A mass flow controllers connected to a MKS 247 power supply operated at constant flow. The pressure was measured utilizing a Baratron MKS Type 622 with a 10 torr range and maintained at 5-6 torr for all measurements.

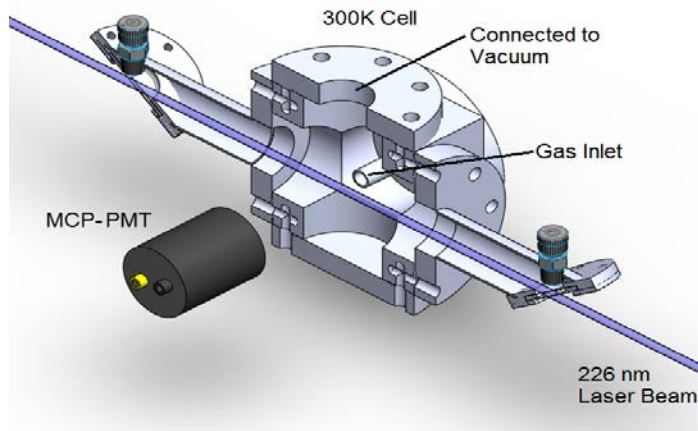


Figure 3: Slow flow cell for 300K experiments <sup>11</sup>

The low temperature measurements were obtained using the RPHT cell as described previously in figure 1. A 25ms pulse was used and the pressure was monitored using an Endevco model 8640-15 piezoresistive pressure sensor. The  $Q_2 + R_{12}$  and  $P_2 + Q_{12}$  bands in the  $A^2\Sigma^+$  ( $v'=0$ )  $X^2\Pi_{1/2}(v''=0)$  transitions were used to measure the temperature. Using ten rotational states a Boltzmann plot was created to monitor the absolute rotational temperature of the rotational peaks.

The gas mixture for both high and low temperature measurements was prepared by mixing 5% NO in  $N_2$  and passing this through a high-pressure bubbler which contained one of the quenchers. The  $C_6H_6$  used was anhydrous and with 99.8% purity and was obtained from Sigma Aldrich. The  $C_6F_6$  was also from Sigma Aldrich. A LabVIEW proportional integral derivative algorithm (PID) was used to maintain the total NO concentration throughout the course of the experiment. The gas mixture was then passed through a cold stainless-steel coil at

286 K in order to control the vapor pressure of the quencher. By varying the total pressure while maintaining a constant pressure of the quencher the concentration of either the  $C_6H_6$  or  $C_6F_6$  can be varied. Absorption measurements were used to confirm that the bubbler was fully saturated with the quencher.

## CHAPTER III

### RESULTS

#### Spectroscopic VENOM

The images obtained from the excitation grid in the VENOM technique were obtained by two stereoscopic cameras which were aligned with respect to a reference camera used for dewarping purposes. The images were an average of 540 shots in order to obtain enough fluorescence intensity. Time delays of 1200 ns and 1800 ns were used for the two probe laser sheets to create enough of a delay to obtain a shift in the flowfield. The flowfield was from left to right.

The warped images collected from the stereoscopic cameras were dewarped with respect to the reference image in order to obtain the out of plane component from a 2D image. Figure 4 shows the PLIF images with (a) and (b) being probed at  $J=8.5$  with a delay of 1200 ns and (c) and (d) being probed at  $J=1.5$  with an 1800 ns delay. Both (a) and (c) were acquired from the top camera and (c) and (d) were obtained from the bottom camera. Images (e) and (f) were obtained using single shot measurements via interline transfer, the former being from the top and the latter being from the bottom. The distinct change in color indicated by the dotted red line denotes the position of the shockwave.

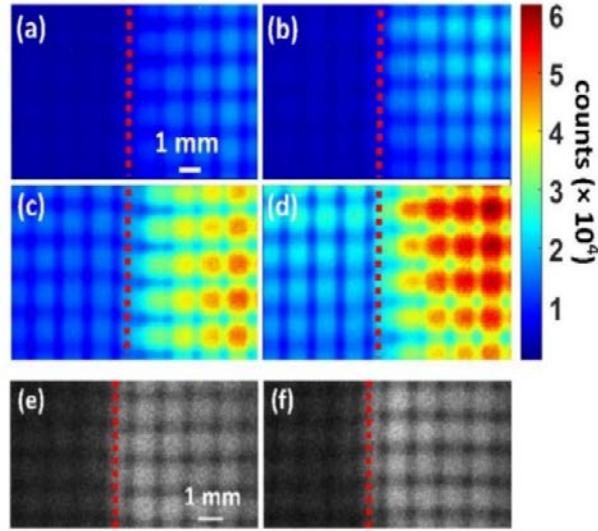


Figure 4: PLIF images used to obtain VENOM velocity and temperature measurements. (a) and (b) are from the top camera, (c) and (d) are bottom camera, and (e) and (f) are single shot.

In the streamwise position after the shockwave the velocity was determined to be  $672 \pm 20$  m/s as opposed to  $760 \pm 14$  m/s preshock. The calculated value was determined to be  $657 \pm 9$  m/s and 739 m/s respectively so these values are consistent with only a 2.8% error. The streamwise value that is calculated is based on the deflection angle of the wedge which was set at 16 degrees. The out of plane velocity, the z axis, was determined to be  $169 \pm 8$  m/s post shock and 0 m/s preshock. The experimental preshock value is consistent within an error of 10% of the calculated value of  $169 \pm 10$  m/s. This is also represented graphically in figure 5.



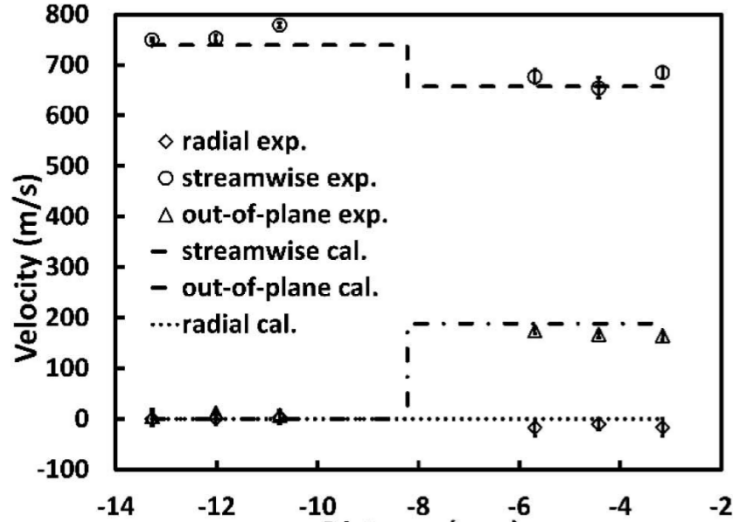


Figure 5: Graphical representation of the CFD calculations as compared to the experimental data<sup>13</sup>

In order to obtain proper velocity measurements, a significant enough displacement is vital for accurate dewarping while still maintaining the ability to obtain temperature measurements from the fluorescence ratios. The temperature measurements were obtained using thermalized vibrationally excited NO ( $X^2\Pi$ ,  $v''=1$ ). The NO molecules experience rotational collisional energy transfer with ground state NO and  $N_2$ . This thermalization requires a few hundred nanoseconds and 10's of collisions.

## Quenching

When studying the quenching of an excited state molecule the fluorescence decay being measured is a function of the spontaneous emission and the quenching. The constant  $k_f$  is the intrinsic rate of fluorescence and  $M$  is the collisional quencher and  $k_{qm}$  is the rate constant for the

$$NO(A^2 \sum^+ \xrightarrow{K_f} NO(X^2\Pi_{\frac{1}{2}}) + h\nu \quad (1)$$

$$NO(A^2 \sum^+ + M \xrightarrow{k_{q,M}} NO(X^2\Pi_{\frac{1}{2}}) + M \quad (2)$$

collisional quencher  $M$  and is temperature dependent. The background decay was linearly fit to the integrated rate law show in the equation below:

$$\ln(I(t) - I_{BG}) = -(k_{total})t = -(k_f + \sum_M k_{q,M}[M])t \quad (3)$$

$I(t)$  is the measured fluorescence signal and  $I_{BG}$  is the signal with the 226 nm pulse off resonance. The logarithmic plots were found to be linear over two orders of magnitude which is indicative of pseudo first order kinetics. The decays were fit starting at a 15 ns time delay after the excitation and extending over 500 decays. A near constant concentration of NO was maintained in over to minimize the effect of the  $k_{q,NO}[NO]$  term and allowing for a linear fit to be obtained with respect to  $[C_6H_6]$  or  $[C_6F_6]$  where the  $k_{total}$  vs  $[M]$  is directly correlated to the  $k_{q,M}$  value. The quenching effects of  $N_2$  can be ignored due to the quenching cross section being ~5000 times smaller than that of NO. A fast response pressure sensor was utilized at the nozzle exit to measure the impact pressure and in turn used to determine the static pressure of the flow for an isentropic flow of a perfect gas in a de Laval nozzle. Condensation of both species was initially a concern, however upon monitoring the temperature spectroscopically, it was confirmed that any condensation that may be present would have no significant impact on the flow.

Measured decay rates at 300 K as a function of the quencher concentration are shown in Figure 6 where the black symbols are for benzene and the red are for C<sub>6</sub>F<sub>6</sub>. The linear fits are shown as dashed lines with the y- intercepts equaling the intrinsic rate of fluorescence and NO self-quenching. Low temperature quenching data is shown in Figure 7 with five concentrations of the quencher measured for each data set collected.

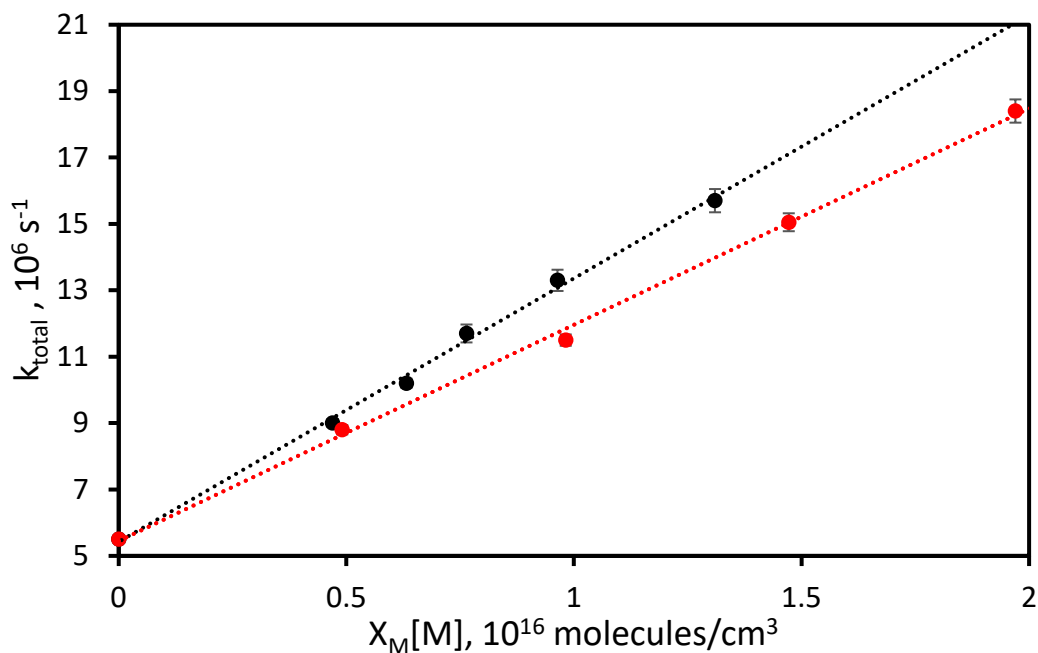


Figure 6: Plot of decay rates at 300K as a function of the quencher concentration <sup>11</sup>

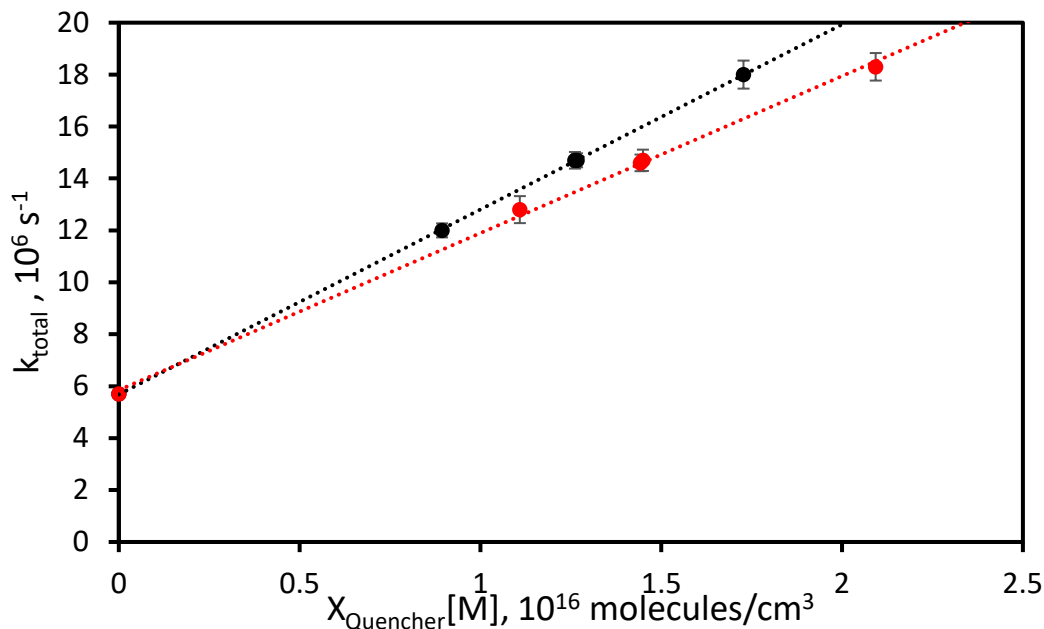


Figure 7: Decay plot at 147K as a function of the concentration of the quencher<sup>11</sup>

Quenching cross sections for each temperature were determined. The temperature behavior is shown graphically in figure 7. The best fit for benzene was determined using equation 4 and optimizing the  $C_0$  and  $C_1$  values via least square analysis.

$$\sigma_Q = C_0 * T^{C_1} \quad (4)$$

The  $C_0$  value was determined to be 842 and the  $C_1$  value to be -0.31 for benzene. For  $C_6F_6$  the values were determined to be 803 and -0.32 respectively. The predicted  $C_1$  value was -0.33 according to the capture cross section model. When this value is fixed the benzene and  $C_6F_6$   $C_0$  values were found to be 954 and 868 respectively. When  $C_1$  is allowed to vary the cross section values were predicted to be  $250 \text{ \AA}^2$  and  $230 \text{ \AA}^2$  for benzene and  $C_6F_6$ .

Using experimentally determined  $k_{q,M}$  values the quenching cross section can be determined and this allows the temperature dependence on the average gas velocity to be removed. The thermally averaged quenching cross sections were determined using equation 5

where  $\mu_{\text{NO},M}$  is the reduced mass, NO,  $k_B$  is the boltzman constant and T is temperature. The calculated values are shown in table 1.

$$\langle \sigma_{q,M} \rangle = k_{q,M} \sqrt{\frac{\pi \mu_{\text{NO},M}}{8k_B T}} \quad (5)$$

A charge transfer mechanism, known as the harpoon mechanism has previously be used to demonstrate the quenching of NO ( $A_2\Sigma^+$ ) for various other molecules including  $\text{CCl}_4$ ,  $\text{CF}_2\text{Cl}_2$  and others. This mechanism assumes the electron affinity of the quencher is high enough to initiate the initial electron transfer where the electron is moving from electronically excited NO to the quencher via tow different curve crossings. This model indicates that species with large negative electron affinity values have negligible cross sections, however this is not consistent with the data shown in table 1.

Table 1: Collisional cross sections, electron affinity, and A-state energy for the species discussed<sup>1-12</sup>

Quenching Species	$k_q$ ( $10^{-10}$ cm <sup>3</sup> /s) at 300 K	$\sigma$ ( $\text{\AA}^2$ ) at 300 K	$\sigma$ ( $\text{\AA}^2$ ) at 130 K	$\sigma$ ( $\text{\AA}^2$ ) at 145 K	$\sigma$ ( $\text{\AA}^2$ ) at 155 K	$\sigma$ ( $\text{\AA}^2$ ) at 177 K	Electron Affinity (eV)	A-state Energy (eV)
NO	NA	30.5–43.5 <sup>b</sup>	48.9 <sup>c</sup>	47.8 <sup>c</sup>	47.1 <sup>c</sup>	45.7 <sup>c</sup>	NA	5.45 <sup>f</sup>
C <sub>6</sub> H <sub>6</sub>	7.93 ± 0.42 <sup>a</sup>	147 ± 9 <sup>a</sup>	186 ± 10 <sup>a</sup>	188 ± 8 <sup>a</sup>	NA	175 ± 8 <sup>a</sup>	−1.5 <sup>d</sup>	4.9 <sup>g</sup>
C <sub>6</sub> F <sub>6</sub>	6.51 ± 0.28 <sup>a</sup>	133 ± 7 <sup>a</sup>	168 ± 13 <sup>a</sup>	172 ± 8 <sup>a</sup>	167 ± 10 <sup>a</sup>	NA	1.2 <sup>e</sup>	4.8 <sup>g</sup>

c From Ref. [14]

d From Ref. [12]

e From Ref. [3]

f From Ref. [16]

g From Ref. [17]

The near resonance electronic energy transfer (RET) model involves electronic energy from NO ( $A_2\Sigma^+$ ) transferring to rotational and vibrational energy levels in the A-state of the

collisional quencher involved. The predictions of the energy rate based on this model is related to the electronic coupling between the donor and acceptor species. In this process, the quencher has an electronically excited state with a lower energy than the NO A-state and is not dependent on the electron affinity. This is consistent with the values presented in table one and the electron affinity values for the quenching molecules discussed here.

When using the RET model a  $T^{-2/3}$  model would typically be predicated based on dipole-dipole interactions and dispersion forces, however since both aromatic species discussed here have no dipole moment the prediction yields a  $T^{-1/3}$  dependence and can be modeled by equation 6. The first term is correlated to temperatures under 300 K and the second term is related to high temperature quenching cross sections. Ignoring the second term to focus on lower temperature data, a  $C_1$  value of -1/3 is predicted and the experimentally determined value is 0.31 which is within 7% of the predicted value.

$$\sigma(T) = C_0 T^{C_1} + c_2 e^{-c_3/T} \quad (6)$$

## CHAPTER IV

### CONCLUSION

The use of stereoscopic VENOM to obtain three component velocity as well as two component temperature is obtained using NO ( $v'' = 1$ ) obtained from spontaneous emission and collisional quenching from the A state. This technique has potential to provide an insight into supersonic and hypersonic challenges facing both chemists and aerospace engineers by providing the experimental data necessary to develop accurate diagnostic techniques.

The collisional cross section of NO ( $A_2\Sigma^+$ ) was able to be successfully determined at both high and low temperatures using time-resolved laser induced fluorescence. The results discussed here vary from predictions using the harpoon mechanism and have been used to describe collisional quenching systems in the past. This model does not accurately predict the large collisional quenching cross section seen in benzene and therefore the near resonant collisional energy transfer mechanism has been proposed. Using this mechanism, a temperature dependence of  $T^{-1/3}$  is predicted for both  $C_6H_6$  and  $C_6F_6$ . In order to further confirm the RET model discussed here it would be beneficial to measure the quenching cross sections of various other quenchers with zero dipole as well as those with a dipole in order to determine if these types of molecules would break the trend.

Developing diagnostic techniques which allow for the measurement of temperature and velocity in a supersonic and hypersonic flight is vital to understanding the energy coupling. Turbulent flowfields represent challenges on both the macro and quantum levels and therefore is of interest to both chemist and engineers. Tackling these challenges from both a computational and experimental lens enables scientists to develop more accurate and effective techniques which

have the potential to reshape the landscape for air travel.



## REFERENCES

- (1) Batley, M.; Lyons, L. E. Electron Affinities of Organic Molecules. *Nature* **1962**, *196*, 573.
- (2) Strickler, S. J. Molecular spectra and molecular structure. Volume 3, electronic spectra and electronic structure of polyatomic molecules (Herzberg, Gerhard). *Journal of Chemical Education* **1967**, *44*, A760.
- (3) Greenblatt, G. D.; Ravishankara, A. R. Collisional quenching of NO(A,  $v' = 0$ ) by various gases. *Chemical Physics Letters* **1987**, *136*, 501-505.
- (4) Wentworth, W. E.; Limero, T.; Chen, E. C. M. Electron affinities of hexafluorobenzene and pentafluorobenzene. *The Journal of Physical Chemistry* **1987**, *91*, 241-245.
- (5) Raiche, G. A.; Crosley, D. R. Temperature dependent quenching of the A  $2\Sigma^+$  and B  $2\Pi$  states of NO. *The Journal of Chemical Physics* **1990**, *92*, 5211-5217.
- (6) Gray, J. A.; Paul, P. H.; Durant, J. L. Electronic quenching rates for NO(A  $2\Sigma^+$ ) measured in a shock tube. *Chemical Physics Letters* **1992**, *190*, 266-270.
- (7) Paul, P. H.; Jr., J. L. D.; Gray, J. A.; Furlanetto, M. R. Collisional electronic quenching of OH A  $2\Sigma$  ( $v' = 0$ ) measured at high temperature in a shock tube. *The Journal of Chemical Physics* **1995**, *102*, 8378-8384.
- (8) Zhang, R.; Crosley, D. R. Temperature dependent quenching of A  $2\Sigma^+$  NO between 215 and 300 K. *The Journal of Chemical Physics* **1995**, *102*, 7418-7424.
- (9) Settersten, T. B.; Patterson, B. D.; Gray, J. A. Temperature- and species-dependent quenching of NO A  $\Sigma^+2(v' = 0)$  probed by two-photon laser-induced fluorescence using a picosecond laser. *The Journal of Chemical Physics* **2006**, *124*, 234308.
- (10) Settersten, T. B.; Patterson, B. D.; Carter, C. D. Collisional quenching of NO A  $\Sigma^+2(v' = 0)$  between 125 and 294 K. *The Journal of Chemical Physics* **2009**, *130*, 204302.

(11) Winner, J. D.; West, N. A.; McIlvoy, M. H.; Buen, Z. D.; Bowersox, R. D. W.; North, S. W. The role of near resonance electronic energy transfer on the collisional quenching of NO ( $A^2\Sigma^+$ ) by C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>F<sub>6</sub> at low temperature. *Chemical Physics* **2018**, *501*, 86-92.

(12) Briegleb, G. Electron Affinity of Organic Molecules. *Angewandte Chemie International Edition in English* **1964**, *3*, 617-632.

(13) Pan, F.; Sanchez-Gonzalez, R.; McIlvoy, M. H.; Bowersox, R. D. W.; North, S. W. Simultaneous three-dimensional velocimetry and thermometry in gaseous flows using the stereoscopic vibrationally excited nitric oxide monitoring technique. *Optics Letters* **2016**, *41*, 1376-1379.

(14) Sanchez-Gonzalez, R.; Bowersox, R. D. W.; North, S. W. Simultaneous velocity and temperature measurements in gaseous flowfields using the vibrationally excited nitric oxide monitoring technique: a comprehensive study. *Applied Optics* **2012**, *51*, 1216-1228.

(15) Sanchez-Gonzalez, R.; Bowersox, R. D. W.; North, S. W. Vibrationally excited NO tagging by NO( $A^2\Sigma^+$ ) fluorescence and quenching for simultaneous velocimetry and thermometry in gaseous flows. *Optics Letters* **2014**, *39*, 2771-2774.